

**PEARLESCENT PIGMENTS BASED ON SELECTIVELY ABSORBING LAYERS OF CHALCOGENIDE, OXYCHALCOGENIDE AND MIXED CHALCOGENIDES**

[0001] The present invention relates to novel pearlescent pigments based on substrates comprising at least one selectively light absorbing layer which consists of a chalcogenide and/or oxychalcogenide, preferably sulfides or oxysulfides excluding rare earth and yttrium sulfides and rare earth and yttrium oxysulfides. The coatings can be directly prepared by the precipitation of chalcogenides in liquid suspension onto the substrates. Preferably, metal oxides or mixed metal oxides are coated onto the substrate; the resulting precursor is transferred into a furnace and calcined under a sulfurizing gas flow to convert the oxides into oxysulfides and/or sulfides depending on the reaction parameters. The conversion to sulfides and/or oxysulfides is preferably carried out in a fluidized bed reactor. Angle-dependent optical pigments are thus produced, which are especially useful in paints, powder coatings, paper coatings, plastics, cosmetics, inks and security-enhancing features as well as in decorative applications for foods and drugs.

[0002] Absorption pigments based on chalcogenide, oxychalcogenide and mixed chalcogenides without a layered or substrate-based structure are well known. A comprehensive overview about these substances can be found in Mane, R.S. and Lokhande, C.D., "Chemical deposition method for metal chalcogenide thin films," *Materials Chemistry and Physics*, 65 (2000), 1-31.

[0003] First attempts to use the advantages of these substances for the production of more sophisticated substrate-based effect pigments are described in US-A 6,063,179. This patent describes goniochromatic luster pigments based on silicon dioxide platelets coated with a non-selectively absorbing film-like layer at least partially transparent to visible light, and if desired an outer layer which consists essentially of colorless or selectively absorbing metal

oxide and/or comprises a phosphate, chromate and/or vanadate. The nonselectively absorbing layer can be a metal sulfide, such as iron, cobalt, nickel, chromium, molybdenum and tungsten sulfide. These layers non-selectively absorb light which results in primarily black or dark colored pigments.

[0004] A layer is selectively absorbing if there is a higher or lower absorption in a certain region of the electromagnetic spectrum. The result is a real color effect different from white-gray-black (Coating (2001)(4) 135; chroma according to DIN 5033 and DIN 6174).

[0005] A number of pigments based on sulfides and oxysulfides are disclosed in DE-A 19 81 03 17 (corresponds to US 6,419,736). Specifically platelet-shaped substrates coated with sulfides having the formula  $M_2S_3$  and oxysulfides having the formula  $M_2S_{3-x}O_x$  ( $0.05 \leq x \leq 2.5$ ) are mentioned in which M is a rare earth element or yttrium. The substrates are chosen from natural and synthetic mica,  $SiO_2$ -,  $TiO_2$ -,  $Al_2O_3$ -flakes, glass flakes, graphite,  $BiOCl$ , kaolin, talc, vermiculite, iron oxide flakes and metal flakes. These substrates may be uncoated or coated with one or more layers of oxides under the sulfide respectively oxysulfide layer. The sulfide respectively oxysulfide layers may be doped with one or more alkali ions, such as Na or K ions. The process for making these pigments comprises coating the substrates with an oxide, an oxide hydrate or an oxalate through a precipitation process. Then the pigments are dried, calcined between 400°C and 800°C and converted into sulfides respectively oxysulfides under S,  $CS_2$ ,  $H_2S$  or a compound containing S. Due to the usage of rare earth elements, these pigments and their production are high priced what limits the usability in applications.

[0006] It was therefore an object of the present invention to provide readily available pigments with a great variety of different mass-tones which combine an viewing angle

dependant interference phenomenon with the absorption color, therewith extending the range of pearlescent pigments based on chalcogenides/oxychalcogenides.

[0007] Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

[0008] The pigments according to the present invention fulfill the above-mentioned objectives. Therefore, the present invention describes pearlescent pigments based on substrates comprising at least one selectively light absorbing layer of chalcogenide and/or oxychalcogenide excluding rare earth and yttrium sulfides and rare earth and yttrium oxysulfides. The term chalcogenide here refers to sulfur, selenium or tellurium compounds. Preferably, the chalcogenide and/or oxychalcogenide is a metal chalcogenide and/or metal oxychalcogenide with a metal being selected from group 2 and/or 4-16 of the periodic system.

[0009] The chalcogenide-, oxychalcogenide- and mixed chalcogenide-containing coatings can be prepared, for example, by the precipitation of chalcogenides onto substrates in liquid suspension onto the substrates. For example, sodium sulfide and a metal chloride are simultaneously added to a suspension of platelet-shaped substrates leading to a hydrous metal sulfide coating onto said substrates. In a similar way, ammonium sulfide, ammonium polysulfide or sodium selenide or sodium telluride can be used. The resulting coated substrate, the so-called precursor, is separated from the mother liquid, dried and preferably calcined. The selenide or telluride main components and dopants can also be precipitated via decomposition or hydrolysis of organic precursors in gas phase, aqueous phase or non-aqueous main phase reactions, e.g. using  $R^1-Se-R^2$  or  $R^1-Te-R^2$  as educts with  $R^1$  respectively  $R^2 = \text{alkyl, aryl, Me}_3\text{Si}$ .

[0010] However, in this invention the preferred synthesis of the new pigments is performed via a two-step process including a gas phase reaction. The first step is the synthesis of a precursor based on a substrate. The second step is a conversion process, carried out in a furnace. The pearlescent pigments according to the present invention can be produced in conventional static ovens, belt kilns or rotary kilns. However, a commercially more attractive product with less agglomerates and faster reaction rates is obtained in fluidized bed reactors.

[0011] In the first step a layer of an oxide, hydroxide, mixed oxide and/or mixed hydroxide is deposited onto a substrate, thus obtaining the precursor being used in the second step. All known deposition techniques, such as aqueous precipitation processes, CVD and/or PVD processes can be used. However, preferably an aqueous precipitation process described for example in US-A 3,087,828, US-A 3,087,829, DE-A 19 59 998, DE-A 20 09 566, DE-A 22 14 545, DE-A 22 44 298, DE-A 23 13 331, DE-A 25 22 572, DE-A 31 37 808, DE-A 31 37 809, DE-A 31 51 343, DE-A 31 51 354, DE-A 31 51 355, DE-A 32 11 602, DE-A 32 35 107, WO 93/08237 and EP-A 0 763 573 is used to obtain the precursor. Halide, carbonate, oxalate, chloride or oxychloride solutions are used to precipitate oxides, hydroxides, mixed oxides and/or mixed hydroxides onto the substrates. The reaction parameters such as temperature, pH, agitation velocity and reactor geometry are optimized to yield a flat continuous layer of the insoluble oxides and/or hydroxides on the substrates. The mixed oxides and/or hydroxides are co-precipitated onto the substrates following an analogous process. Solutions of the different metal salts are mixed and then slowly added in the reactor to coat the substrate. The oxide, hydroxide, mixed oxide and/or mixed hydroxide can be doped with metal ions, silicon oxide, aluminum oxide, boron oxide, sulfur, phosphate

ions and/or sulfate ions. The dopants can be used to create color effects (like rare earths, vanadium, or cobalt ions) as well as for the control of grain growth (like  $\text{SiO}_2$  or aluminum oxide) during the subsequent second step. For the latter purpose, for example, small amounts sodium silicate or soluble borates can be added to the coating solution via the metal salt or the acidic respectively caustic solutions that are used to adjust the pH. Examples of metal ions as dopant are silicon, vanadium, chromium, aluminum, cerium, neodymium, praseodymium, selenium, cobalt, nickel and/or zinc ions, preferably vanadium and/or cobalt ions.

**[0012]** Substrates that can be used in the present invention as base material on which the oxides, hydroxides, mixed oxides and/or mixed hydroxides are precipitated include platelet-shaped, spherical or needle-shaped substrates. Preferably the substrates comprise but are not limited to:

**[0013]** Platelets: Micaceous iron oxide, natural (for example as in WO 99/48634), synthetic or doped (for example as in EP-A 0 068 311) micas (muscovite, phlogopite, fluorophlogopite, synthetic fluorophlogopite, talc, kaolin), basic lead carbonate, platelet-shaped barium sulfate,  $\text{SiO}_2$ -,  $\text{Al}_2\text{O}_3$ -,  $\text{TiO}_2$ -, Glass-,  $\text{ZnO}$ -,  $\text{ZrO}_2$ -,  $\text{SnO}_2$ -,  $\text{BiOCl}$ -, chromium oxide-,  $\text{BN}$ -,  $\text{MgO}$ -flakes,  $\text{Si}_3\text{N}_4$ , graphite, pearlescent pigments (including those which react under the fluidized bed conditions to nitrides, oxynitrides or by reduction to suboxides etc.) (for example EP-A 9 739 066, EP-A 0 948 571, WO 99/61529, EP-A 1 028 146, EP-A 0 763 573, US-A 5,858,078, WO 98/53012, WO 97/43348, US-A 6,165,260, DE-A 15 19 116, WO 97/46624, EP-A 0 509 352), pearlescent multilayer pigments (for example EP-A 0 948 572, EP-A 0 882 099, US-A 5,958,125, US-A 6,139,613) and/or metals. Preferably, the metal is aluminum and/or titanium, most preferably passivated by inorganic treatment.

[0014] Spheres: coated SiO<sub>2</sub> spheres (for example EP-A 0 803 550, EP-A 1 063 265, JP-A 11 322 324), uncoated SiO<sub>2</sub> spheres (Ronaspheres<sup>®</sup>, all spheres described as starting materials in EP-A 0 803 550, EP-A 1 063 265, JP-A 11 322 324), micro bubbles (US-A 4,985,380).

[0015] Needle-shaped metal oxides: preferably iron oxide.

[0016] The size of the substrates is not critical. The mean diameter of the substrates and hence the resulting pigments preferably varies between 1 and 500 µm, more preferably 5 and 50 µm. Preferably, the mean diameter in the case of, for example, the platelet-shaped substrates can vary between 5 and 200 µm, more preferably between 10 and 150 µm. The mean diameter of the spherical substrates preferably varies between 10 nm and 100 µm, more preferably between 500 nm and 50 µm and most preferably from 1 to 20 µm. Such substrates are commercially available or can be obtained by known processes.

[0017] The chalcogenide and/or oxychalcogenide layer can be coated directly onto the substrate as described above. In the same way nitride respectively oxynitride layer coated substrates can be used as substrates to precipitate an optical layer(s) as described above.

[0018] In the second step for the production of pigments according to the present invention, the oxides, hydroxides, mixed oxides and/or mixed hydroxides obtained in the above described first step are converted into chalcogenides and/or oxychalcogenides. This can be achieved by calcination of the precursor obtained in the first step in conventional static ovens, belt kilns or rotary kilns. However, a better product with less agglomerates and faster reaction rates is obtained in fluidized bed reactors. This process can be performed batchwise or continuously. The conversion is carried out with a reactive gas, which may consist of H<sub>2</sub>S, CS<sub>2</sub>, sulfur and/or a mixture of these. Additionally an inert gas, such as Ar or N<sub>2</sub>, preferably

N<sub>2</sub>, may be present during the conversion. The gas composition preferably varies from >0 to 100 vol-%, more preferably from 20 to 80 vol-%, of reaction gas in inert gas.

**[0019]** The temperature is maintained at a fluidized bed temperature of preferably about 700-1250°C, more preferably 800°C to 1100°C. The conversion of oxides, hydroxides, mixed oxides and mixed hydroxides to chalcogenides and/or oxychalcogenides is carried out depending on the different parameters, such as gas flow rates, reaction time or temperature profiles. The longer the reaction time the higher the chalcogenide-to-oxychalcogenide ratio. Consequently the reaction time determines the obtained structure of the compound. The color and the color strength of the pearlescent pigments according to the present invention is associated to a determined structure; thus, the reaction time is preferably well controlled. In addition, for the same reason, good temperature control is desired. The control and optimization of the process parameters can be performed in a manner known in the art.

**[0020]** In order to maintain the almost ideal conditions prevalent in a homogeneous fluid bed in countercurrent/cocurrent contact, special devices to achieve such contact may be used. Instabilities, like formation of channels or of bubbles in the bed, can be lessened or eliminated by use of vibration or agitating components.

**[0021]** If the reaction with the reaction gas is not carried out to full completeness, mixtures of phases can be obtained including layers with a gradient of phase concentration through the layer thickness. These incompletely reacted products can be advantageous with respect to a desired color shade.

**[0022]** The thickness of the chalcogenide and/or oxychalcogenide layers preferably varies between 5 and 500 nm, yielding slight shades and flat angle color effect at low thickness and

very pronounced hiding at high thickness. For the optimal interference effect, the preferred thickness is 50-350 nm, especially preferred 80-200 nm.

[0023] The interference color is determined by the optical thickness, which is the geometrical thickness of the layer multiplied by the refractive index (Pfaff, G.; Reynders, P. “Angle-dependent optical effects deriving from submicron structures of films and pigments,” *Chemical Review*, 99 (1999), p.1963-1981). The latter is a strong function of the chosen material but is in general not known for the new materials mentioned in this invention. The mass tone of the absorbing pigments is, as well, a function of the layer thickness. Therefore, the desired color effect is empirically optimized by adjustment of the amount of precursor, i.e., controlling the precursor layer thickness, and regulation of the conversion reaction with the reactive gases.

[0024] Preferably, the selectively light absorbing layer of chalcogenides and/or oxychalcogenides may consist of:

Sulfides:

1. Sulfides containing one metal:
  - $A_xS_y$  with  $A = \text{Zr, Fe, Zn, Mn, Co, Ni, Cu, In, Sn, Pb, Ag, Bi, Sb, As, Cr, Mo, W, Rb, Ti}$   
 $x > 0, y > 0$   
such as  $\text{ZnS, FeS}_2, \text{Fe}_3\text{S}_4, \text{MoS}_2$
  - $A_xS_y$  doped with Ag, Al, Au, Cu, Eu, Sm or a mixture of these cations, such as  $\text{ZnS:Ag, ZnS:Al, ZnS:Au, ZnS:Cu, ZnS:Cu or Al, ZnS:Cu or Al or Au, SrS:Eu or Sm, SrS:Ce or Sm, SrS:Cu}$  and with  $x > 0, y > 0$



- $A_xS_y$  doped with  $Eu_m$ ,  $Tr_n$  and  $O_pX_q$   
with A = alkaline earth metal ion,  
Tr = one or more trivalent rare earth metal ions,  
X = halide,  
 $0.01 < m < 0.5$ ,  $0.01 < p < 2$ ,  $0.01 < q < 0.5$  (values in atomic percent), or m, n, p, q are integers,  
such as  $SrS:Eu:Er:OCl$ ,  $SrS:Eu_{0.1}:Er_{0.1}:Dy_{0.1}:OCl$
  
- 2. Sulfides containing two or more metals:  
  
 $CuInS_2$ ,  $CuBiS_2$ ,  $CuFeS_2$ ,  $Rb_4Ta_2S_{11}$ ,  $CuPrS_2$ ,  $Nd_2TeS_2$   
  
 $EuCe_2S_4$ ,  $CaLa_2S_4$ ,  $Cu_5FeS_4$ ,  $CuCr_2S_4$ ,  
  
 $Pb_xCa_{1-x}La_2S_4$ ,  
such as  $Pb_{0.1}Ca_{0.9}La_2S_4$ ,  $PbCeS_4$
  
- $Na_4SiS_{10}$ ,  $Ce_3Si_2IS_8$ ,  $ZnSeS$ ,  $ZnSe_{0.53}S_{0.47}$ ,  $TlSeS$ ,  $K_4Nb_2S_{10}$ ,  $K_6Nb_4S_{25}$
  
- $Zn_{3-3x}In_{2xy}Ga_{2x-2xy}S_3$   
with  $0.2 < x < 0.97$ ,  $0.1 < y < 1$
  
- $ZnIn_2S_4$ ,  $Zn_2In_2S_5$

- $A_6Nb_4S_{22}$   
with  $A = Rb, Cs$   
 $CuGa_5S_8, CuIn_5S_8$
- $AgGa_xIn_{5-x}S_8$  with  $0 < x < 3$ ,  
such as  $AgGa_3In_2S_8, AgGa_5S_8, AgIn_5S_8, AgGa_4InS_8$
- $Rb_4Ti_3S_{14}, Cs_4Zr_3S_{14}, K_4Ti_3S_{14}, Tl_2TiS_4, Cs_2TiS_3, K_2TiS_3, Na_2ZrS_3, Ba_3Zr_2S_7,$   
 $Cu_2HfS_3, Cu_4TiS_4, Ag_4Hf_3S_8, Ag_2HfS_3$
- $KLnMS_4$   
with  $Ln = \text{rare earth or Y}$ ,  
 $M = Si, Ge$ ,  
such as  $KCeSiS_4, KLaGeS_4$
- $Ca_{(1-x)}Yb_{(2/3 x)}\text{Defect}_{(1/3 x)}S$  with  $0 < x < 1$

Oxysulfides:

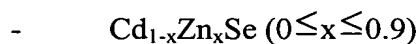
- $ZrOS, Rb_4Nb_2OS_{10}$   
 $Na-Sr-Cu-M-O-S$   
with  $M = Zn, Ga, In$   
preferably  $Sr_{2-x}Na_xCu_2ZnO_2S_2, Sr_{2-x}Na_xCuGaO_3S$  with  $x > 0$ ,  $Sr_2Cu_2ZnO_2S_2,$   
 $Sr_2CuGaO_3S, Sr_2CuInO_3S$

Selenides:



with A = Cd, Zn, Bi, Sb, Ni, Tl, Pb, Cu, Mo, Sn, Co, with  $x > 0$ ,  $y > 0$

such as ZnSe, Bi<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>Se<sub>3</sub>, NiSe, TlSe, PbSe, CuSe, MoSe<sub>2</sub>, SnSe, CoSe



Sulfoselenides:



[0024] The new pearlescent pigments described herein can be used as a substrate to precipitate further optical layers thereon. If desired, the pigments according to the present invention can be further coated with one or more layers of metal oxides, metal oxide hydrates, metal fluorides and/or semitransparent metal layers on top of the selectively light absorbing layer. The selectively light absorbing layer can also be placed as an intermediate layer of metal oxide, metal oxide hydrate, metal fluoride and/or semitransparent metal stacks. The metal oxide can be selected from any metal oxide, preferably from titanium oxide, iron oxide, aluminum oxide, aluminum oxide hydrate, silicon oxide, silicon oxide hydrate, zirconium

oxide, chromium oxide, zinc oxide, tin oxide, antimony oxide, indium oxide, potassium ferric ferro cyanides, most preferably from titanium oxide, iron oxide, aluminum oxide, aluminum oxide hydrate, silicon oxide, silicon oxide hydrate and/or mixtures thereof. The metal fluoride is preferably magnesium fluoride. The metal of the semitransparent metal layer can be selected from chromium, molybdenum, aluminum, silver, platinum, nickel, copper and/or gold, preferably from aluminum, silver. In particular, the metal oxide, metal oxide hydrate, metal fluoride and/or semitransparent metal layers are arranged as alternating layers of metal oxide, metal oxide hydrate, metal and/or metal fluoride with a refractive index  $n > 1.8$  and a metal oxide, metal oxide hydrate, metal and/or metal fluoride with a refractive index  $n < 1.8$ . Pigments according to this embodiment combine the color of the complex phosphate system with an intensively lustrous appearance and may show an angle-dependent interference color.

**[0025]** Preferred examples for metal oxides, metal oxide hydrates and/or metals with a refractive index  $n > 1.8$  are titanium oxide, iron oxide, iron titanate, iron, chromium, silver and/or nickel, preferably titanium oxide, iron oxide, iron titanate.

**[0026]** Preferred examples for metal oxides, metal oxide hydrates, metals and/or metal fluorides with a refractive index  $n < 1.8$  are silicon oxide, silicon oxide hydrate, aluminum oxide, aluminum oxide hydrate, aluminum and/or magnesium fluoride.

**[0027]** Furthermore, the resulting pigments can be coated with inorganic and/or organic compounds to increase their weather stability respectively their photostability. Useful methods are for instance described in US-A 4,134,776, EP-A 0 649 886, WO 97/29059 and references cited therein.

**[0028]** An advantage of this invention is the combination of a great variety of mass-tones of the chalcogenides and derived compounds with an angle dependent interference color that

is adjusted by the layer thickness of the chalcogenide/oxychalcogenide-containing layer. The applications of these new pigments are numerous, such as paints, powder coatings, paper coatings, plastics, cosmetics, inks and security-enhancing features as well as in decorative applications for foods and drugs due to the use of mainly nontoxic materials.

**[0029]** To create new color effects in all applications, the pearlescent pigments according to the present invention can be employed in admixture with filler pigments or transparent and hiding white, colored and black organic and inorganic pigments and also with conventional transparent, colored and black luster pigments based on metal oxide coated mica,  $\text{TiO}_2$  flakes,  $\text{SiO}_2$  flakes or  $\text{Al}_2\text{O}_3$  flakes and coated or uncoated metal pigments,  $\text{BiOCl}$  pigments, platelet-shaped iron oxides or graphite flakes. The inventive pigments can be further coated with organic or inorganic layers to yield combination pigments.

**[0030]** Some layers of the pigments described in this invention have fluorescent, photoluminescent or electroluminescent properties, e.g. rare-earth doped  $\text{ZnS}$  layers. If such a time-delayed color effect is desired, for example in the field of security, optical, projections screen, safety or similar applications, and the inherent property of the invented pigments is not strong enough, physical mixtures of the invented pigments with conventional inorganic or organic fluorescent respectively luminescent pigments can be used.

**[0031]** The entire disclosure of all applications, patents and publications, cited herein and of corresponding European application No. 03002302.2 filed February 3, 2003 is incorporated by reference herein.

**[0032]** The pigments and their production process according to the present invention is more illustratively demonstrated but not limited by means of the following examples.

**EXAMPLES:**

[0033] Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

[0034] In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

Example 1:

[0035] 100 g of muscovite mica (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) are suspended in 2 liters of fully deionized water. The suspension is heated to 75°C. 467 ml of a  $\text{FeCl}_3$  solution is diluted to 1000 ml with water and is slowly added to the reactor. The pH of the solution is kept at pH 3.1 by addition of 15% aqueous sodium hydroxide solution. The preparation is filtered off, washed with completely deionized water, dried at 110°C for 12 hours and calcined at 800°C for 30 minutes. As a result, 70 g of  $\text{Fe}_2\text{O}_3$  are precipitated onto 100 g of mica. This pigment is then put into a fluidized bed reactor, calcined under  $\text{H}_2\text{S}$  at 900°C during 12 hours. A yellow to golden  $\text{FeS}_2$ /mica pigment is obtained.

Example 2:

[0036] 100 g Iriodin<sup>®</sup> 504 ( $\text{Fe}_2\text{O}_3$ /mica, Merck KGaA) are suspended in 2 liters of fully deionized water. The suspension is heated to 75°C. A  $\text{ZrOCl}_2$  solution (72.3 g diluted in 600ml water) is slowly added to the reactor. The solution is kept at pH 3 by simultaneous addition of 15% aqueous sodium hydroxide solution. The preparation is filtered off, washed

with completely deionized water and dried at 110°C for 12 hours. As a result, 50 g of  $\text{ZrO}_2$  are precipitated onto 100 g of Iridin<sup>®</sup> 504. The pigment is then put into a fluidized bed reactor. The precursor is fluidized with  $\text{N}_2$  to 750-850°C and then is treated with  $\text{H}_2\text{S}$  for 360 minutes. A pigment with a reddish golden color (mixed iron sulfide) and a yellow shade (zirconium oxysulfide) is obtained.

Example 3:

[0037] 100 g  $\text{SiO}_2$  flakes (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) are suspended in 2 liters of fully deionized water. The suspension is heated to 75°C. A  $\text{ZrOCl}_2$  solution (72.3 g diluted in 600 ml water) is slowly added into the reactor. The solution is kept at pH 3 by addition of 15% aqueous sodium hydroxide solution. The preparation is filtered off, washed with completely deionized water, dried at 110°C for 12 hours. As a result, 50 g of hydrous  $\text{ZrO}_2$  are precipitated onto 100 g of  $\text{SiO}_2$  flakes. The pigment is then put into a fluidized bed reactor. The precursor is fluidized with  $\text{N}_2$  to 750-850°C and then is converted with  $\text{H}_2\text{S}$  for 360 minutes. A pigment with a yellow color (zirconium oxysulfide) is obtained.

Example 4:

[0038] 50 g of  $\text{ZrO}_2\text{:VCl}_3$ (10:1wt.-ratio) are precipitated onto 100 g of  $\text{SiO}_2$ -flakes (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) using a  $\text{ZrOCl}_2$  solution (72.3 g of  $\text{ZrOCl}_2$  solution containing 7.2 g of  $\text{VCl}_3$  diluted into 600 ml of water) as described in the example 3. The dried pigment is then put into the fluidized bed, calcined at 800°C under  $\text{H}_2\text{S}$  for 360 minutes. A pigment with a blue color (vanadium-doped zirconium oxysulfide) was obtained.

Example 5:

[0039] A metallized zirconium oxysulfide pigment is produced by thermally decomposing chromium hexacarbonyl in the presence of heated zirconium oxysulfide coated onto SiO<sub>2</sub> flakes as described in the example 3. This pigment is fluidized with nitrogen to achieve and maintain a non-bubbling fluidized bed and an oxygen free atmosphere. Then the reactor is heated to 400–450°C and kept under this condition throughout the following coating process. A stream of nitrogen loaded with chromium hexacarbonyl is prepared by passing nitrogen through a flask containing chromium hexacarbonyl, which is kept at 80°C, and introduced subsequently into the reactor. The vaporized compound is passed into the tube for about 90 minutes. About 5 nm of chromium is deposited on the zirconium oxysulfide pigment based onto SiO<sub>2</sub> flakes, forming a semitransparent layer. The organic by-product of the decomposition reaction is separated from the pigment into a scrubber.

Example 6:

[0040] 100 g of muscovite mica (Merck KGaA, diameter 10-50  $\mu$ m) are suspended in 2 liters of fully deionized water. The suspension is heated to 75°C. A ZnCl<sub>2</sub> solution (84 g) is mixed with a CuCl<sub>2</sub> solution (10 g) and the mixture is slowly added to the reactor. The solution is kept at pH 3 by addition of 15% aqueous sodium hydroxide solution. The preparation is filtered off, washed with completely deionized water, dried at 110°C for 12 hours and then calcined at 850°C for 30 minutes. As a result, 50 g of ZnO:Cu are precipitated onto 100 g of mica. This pigment is then put into a fluidized bed reactor, calcined under H<sub>2</sub>S at 1000°C during 12 hours. A blue ZnS:Cu/mica pigment is obtained.



Example 7:

**[0041]** 100 g of silica flakes (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) are suspended in 2 liters of fully deionized water. The suspension is heated to 65°C. A solution of 83 g  $\text{ZnSO}_4$  (120 g/l Zn) containing 0.01 mol%  $\text{CuSO}_4$  is slowly added simultaneously with a solution of 40 g  $\text{Na}_2\text{S}$  (60 g/l  $\text{Na}_2\text{S}$ ) into the reactor. The solution is kept at pH 3.5 by addition of dilute hydrochloric acid solution. The pH is increased to 7 and another small quantity of  $\text{Na}_2\text{S}$  is added in the reactor. The preparation is filtered off, washed with completely deionized water, dried at 130°C for 12 hours and then calcined at 900°C for 120 minutes. As a result, a white zinc sulfide containing pigment is obtained showing luminescence.

Example 8:

**[0042]** 100 g of muscovite mica flakes (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) are suspended in 2 liters of fully deionized water. The suspension is heated to 75°C. A solution of 67.2 g  $\text{SbCl}_3$  diluted with 200 g 32%  $\text{HCl}$  is slowly added simultaneously with a solution of 34.54 g  $\text{Na}_2\text{S}$  into the reactor. The solution is kept at pH 3.5 by addition of dilute hydrochloric acid solution. The preparation is filtered off, washed with completely deionized water, dried at 110°C for 12 hours and then calcined at 450°C for 60 minutes. As a result, an orange antimony(III) sulfide containing pigment is obtained.

Example 9:

**[0043]** 100 g of silica flakes (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) are suspended in 2 liters of fully deionized water. The suspension is heated to 65°C. A solution of 67 g  $\text{ZnSO}_4$  (120 g/l Zn) containing 0.01 mol%  $\text{CuSO}_4$  is slowly added simultaneously with a solution of 16 g  $\text{Na}_2\text{S}$  (60 g/l  $\text{Na}_2\text{S}$ ) and 26 g  $\text{Na}_2\text{Se}$  into the reactor. The solution is kept at pH 3.5 by

addition of dilute hydrochloric acid solution. The pH is increased to 7 and another 0.5 g Na<sub>2</sub>S is added in the reactor. The preparation is filtered off, washed with completely deionized water, dried at 130°C for 12 hours and then calcined at 600°C for 120 minutes. As a result, a white zinc sulfoselenide containing pigment is obtained.

**[0044]** The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

**[0045]** From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.